

# ON LINE MEASUREMENT OF OXYGEN: REVIEW AND NEW DEVELOPMENTS

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## KEYWORDS

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## ABSTRACT

Oxygen is vitally important to the existence of animal life, not only for respiration, but also for the many aspects of the combustion reaction (power generation, vehicular movement, heating) and process control, safety and quality. Continuous measurement techniques are correspondingly important and very specialized. The ability of zirconium oxide to conduct oxygen ions at high temperatures has enabled specific measurement in situ in combustion processes. Less studied and understood have been the older established paramagnetic properties of oxygen and the more recent near infrared absorption enabling measurement via tunable diode lasers. These analytical methods are both related to the unusual electronic structure of the oxygen molecule.

## BACKGROUND

Lavoisier, a chemical revolutionary, bequeathed the name Oxygen and finally established that oxygen was the reactive component of air (Ref. 1). He famously demonstrated the combustion reaction by vaporizing the Holy Emperor's diamonds, forming carbon dioxide, in an early example of the worlds most useful, although now increasingly worrying, chemical reaction.

The exothermic reaction of oxygen with hydrocarbons drives the planet's land, sea and air-based vehicles and provides heat and power for industrial and domestic use.



Additionally, animal life uses the same reaction to create energy.

Humanity is a collection of more than 6 billion mobile combustors, which regularly consume complex hydrocarbon fuels to produce energy, carbon dioxide and water via a controlled combustion process. The growth of civilization then inevitably increases the atmospheric level of carbon dioxide, which via radiative transfer increasingly absorbs heat reflected from the earth's surface. Humanity alone consumes around 2.8 million tons daily of O<sub>2</sub> just from respiration. (Ref 2,3)

A major need to measure O<sub>2</sub> derives from optimizing the combustion process.

The air required for the oxidation of hydrocarbons, usually fossil fuels, is ideally minimized to ensure that fuels are completely oxidized but that undue excess air does not carry away through a flue stack heat that is required for the process. Conventionally, then, excess O<sub>2</sub> is measured in stack gas and the air/fuel ratio to the combustor controlled to the ideal minimum O<sub>2</sub> value. In industry O<sub>2</sub> is also measured to ensure minimize runaway combustion (explosions) to control product formation and optimize quality (e.g. minimize scale formation in metals manufacture).

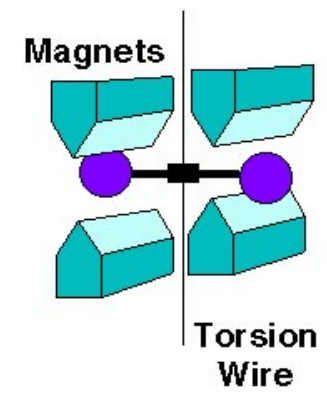
## **PARAMAGNETIC ANALYZERS**

One of the first signs that O<sub>2</sub> is a little odd was reported in 1891 by the Scottish Chemist Sir James Dewar, who found that oxygen was magnetic and managed to attract liquid oxygen to the poles of a magnet. Robert Mulliken (Ref 4) finally explained why oxygen was magnetic using recently developed quantum theory. He showed that molecular oxygen has two unpaired electrons (i.e. the magnetic fields associated with a spinning electron did not cancel out as with paired spins). These electrons dominate the chemistry of oxygen and the occurrence of this "triplet oxygen" as the normal form of O<sub>2</sub>, which finds it hard to receive a bonding pair of electrons and is consequently not an exceptionally reactive molecule, is a convenient fact for animal life. Singlet oxygen, the non-magnetic version with no unpaired electrons, is highly reactive with organic molecules and consequently not compatible with life on this planet (Ref 3, 4). The use of lasers to measure O<sub>2</sub> concentration discussed later involves interaction between triplet and singlet O<sub>2</sub>.

Oxygen's unusual paramagnetic properties enable a relatively specific measurement method, which has been used by industry for approximately fifty years and has been used in three different ways.

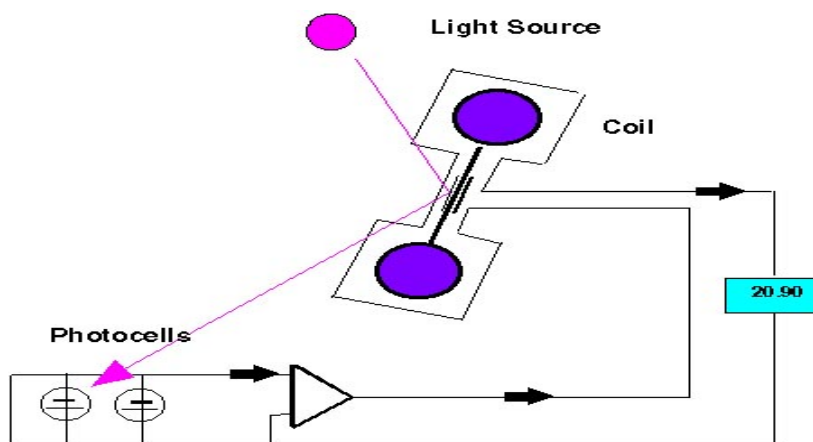
## **DUMBELL OR MAGNETODYNAMIC METHOD**

Two spheres, highly matched in weight and volume, are filled with nitrogen and suspended on a fine platinum wire between in a magnetic field. The nitrogen /glass combination is slightly diamagnetic and repelled by the field (Figure 1).



**FIGURE 1. THE DUMBBELL**

Oxygen flowing through the system causes greater deflection of the dumbbell, the field strength increase and consequent deflection being proportional to the concentration of oxygen. The methodology usually employs a mirror fixed between the spheres. The deflection of a light source reflected from the mirror to twin photocells enables a current arranged to compensate for the potential twist to flow in a wire arranged around the dumbbell (Figure 2). The compensating current is proportional to the O<sub>2</sub> concentration.



**FIGURE 2. MAGNETODYNAMIC METHOD**

The dumbbell is a precisely engineered device which requires relatively low sample flows and pressures but most importantly a clean sample – condensation or particulate formation on the dumbbell or mirror affects the accuracy and may irreparably damage the measuring cell (see Figure 3).

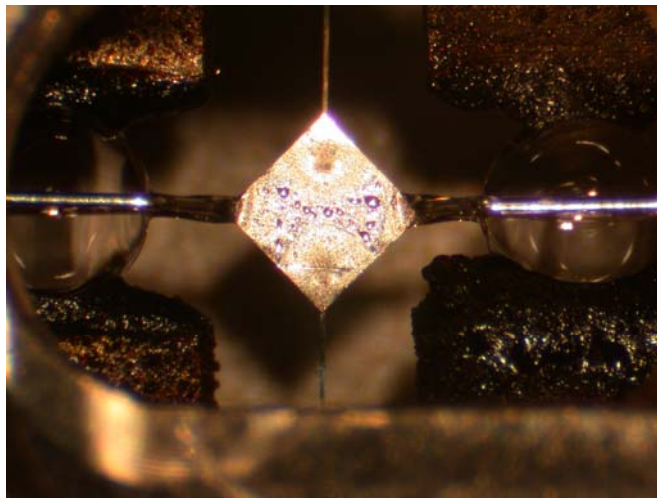
## OTHER PARAMAGNETIC METHODS

The thermomagnetic (or “magnetic wind” method is a simpler mechanism whereby sample gas flows in equal volumes through either side of an annular cell, the sides being connected by a tube around which a wire winding enables a magnetic field, which encourages oxygen to flow through it. The wire winding is organized in a Wheatstone bridge arrangement, flow induced resistance changes being proportional to the O<sub>2</sub> concentration. A variation on this, the magnetopneumatic or “Quinke” method, also uses an asymmetric field to cause oxygen to deviate from its path but the O<sub>2</sub> pressurizes a pressure or flow detector via a reference gas which minimizes contact between sample gas and sensing elements.

The paramagnetic nature of O<sub>2</sub> is a relatively weak effect and POAs are percent measurement devices with at best LDL of 100 ppm under optimum circumstances.

The magnetic nature of triplet O<sub>2</sub> decreases as the temperature rises and consequently POAs are less commonly used in “hot wet” mode.

Dumbbell analyzers have been historically limited to maximum operating temperatures of about 120 degrees C and are only infrequently used in temperatures above 60 C. The non-contact Quinke method has managed temperatures up to 15 degrees C higher than the dumbbell.



**FIGURE 3. DUMBBELL O<sub>2</sub> USED ON SULFUR RECOVERY APPLICATION**

## ZIRCONIA ANALYZERS

Stack gas or waste combustion gas analysis is a traditionally difficult gas analysis application, the degree of difficulty increasing with the molecular weight (and sulfur content) of the fuel. It contains all the unattractive properties of a sample from the viewpoint of a paramagnetic device.

It is hot, wet and often particulate laden and corrosive. Extractive paramagnetic oxygen measurements consequently require highly reliable sample conditioning systems.

The advent of in-stack or at-stack zirconia analyzers in the late 1960's represented a significant change rapidly accepted in industries (HPI, Power) which are traditionally conservative with regard to new technologies.

Figure 4 illustrates the principle. Zirconium oxide (Zirconia,  $ZrO_2$ ) contains interstitial holes, which allow the passage of  $O_2^-$  ions through the ceramic material.

Platinum-coated  $ZrO_2$  heated to temperatures above, typically, 650 degrees C allows the formation of oxygen ions. Differential concentrations of  $O_2$  at electrodes on either side of the ceramic enable a potential difference as described by the Nernst equation where

$$E = \frac{RT}{4F} \ln \frac{O_1}{O_2}$$

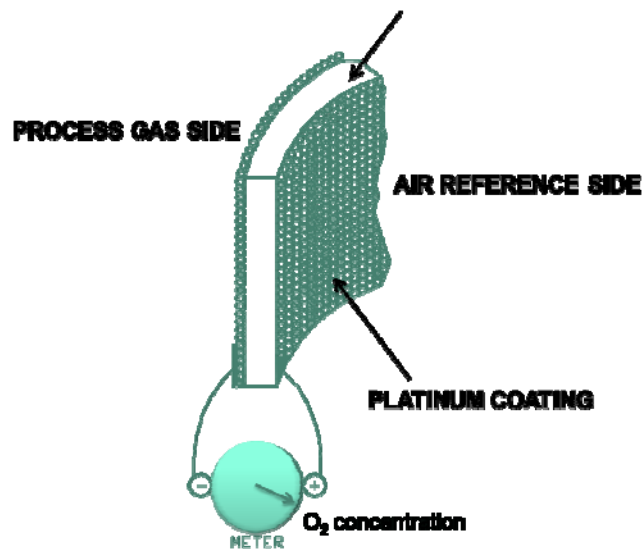
Where E = potential difference

Where R = universal gas constant

Where T = absolute temperature

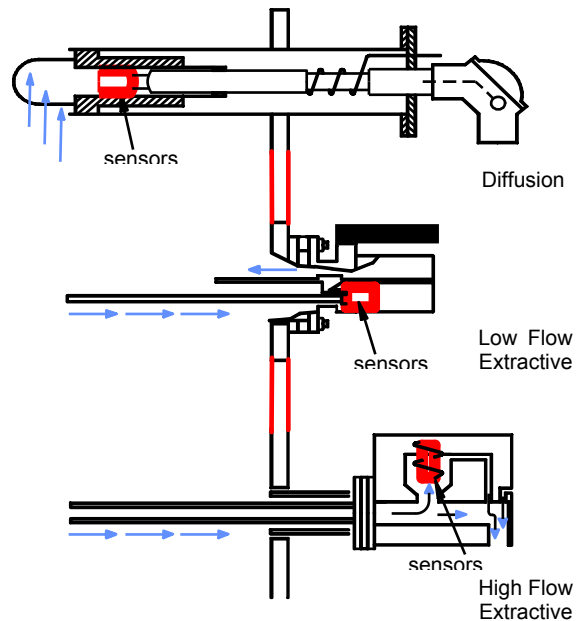
Where F = Faraday constant

A fixed concentration of oxygen (normally air  $O_2$ ) at one electrode enables the evaluation of oxygen concentration at the other ( $O_1$ ).



**FIGURE 4. ZIRCONIA PRINCIPLE**

The inert materials of construction and high temperature of operation make zirconia sensors very applicable for stack gas monitoring. They are applied in one of two ways, either directly in situ or close coupled to the stack. (Figure 5)



**FIGURE 5. ZIRCONIA PROBE INSTALLATION OPTIONS**

The feature which benefits Zirconia for the combustion application, its high temperature of operation, tends to restrict it from most other applications. Measurement of oxygen in a mixture containing any combustible material results on combustion on the catalytic and high temperature surface of the zirconia sensor. It is consequently a “net of combustibles” measurement.

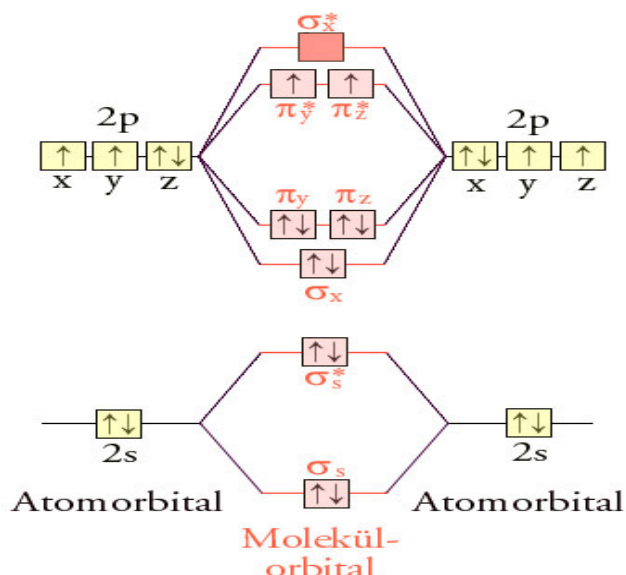
## **TUNEABLE DIODE LASER ANALYZERS (TDL)**

Over the past several years, TDLs have gained much attention for use in industrial applications. Three key attributes of the technique are responsible: specificity for the analyte, high sensitivity, and fast response speed. A TDL’s specificity is the result of the extremely high spectral resolution achievable. Emission bandwidths for tunable diode lasers are on the order of  $10^{-4} - 10^{-5} \text{ cm}^{-1}$ , which results in the ability to isolate a single rotational -vibrational transition line of an analyte species. A second advantage of the TDL is the ability to rapidly tune the lasers, so techniques like wavelength modulation spectroscopy (WMS), which yield dramatic sensitivity enhancements over a direct absorption approach, are easily implemented. Because TDL spectroscopy is an optical technique, it also offers a very fast response time. (Ref. 5, 6, 7)

TDLs are currently mostly used in the near infrared (IR) (< 2.5 microns) region of the electromagnetic spectrum. The availability of these tunable lasers operating at around room temperatures derives from their usefulness in the telecommunications industry. Near IR absorptions are usually overtones of primary absorptions found in the mid IR (2-15 microns) and are relatively weak in intensity compared to mid IR absorptions.

Molecular infrared absorption is associated with asymmetric molecules ,i.e. molecules with at least two different types of atom ,which enable an unevenly distributed chemical bond and a consequent dipole, that interacts with the electromagnetic field.

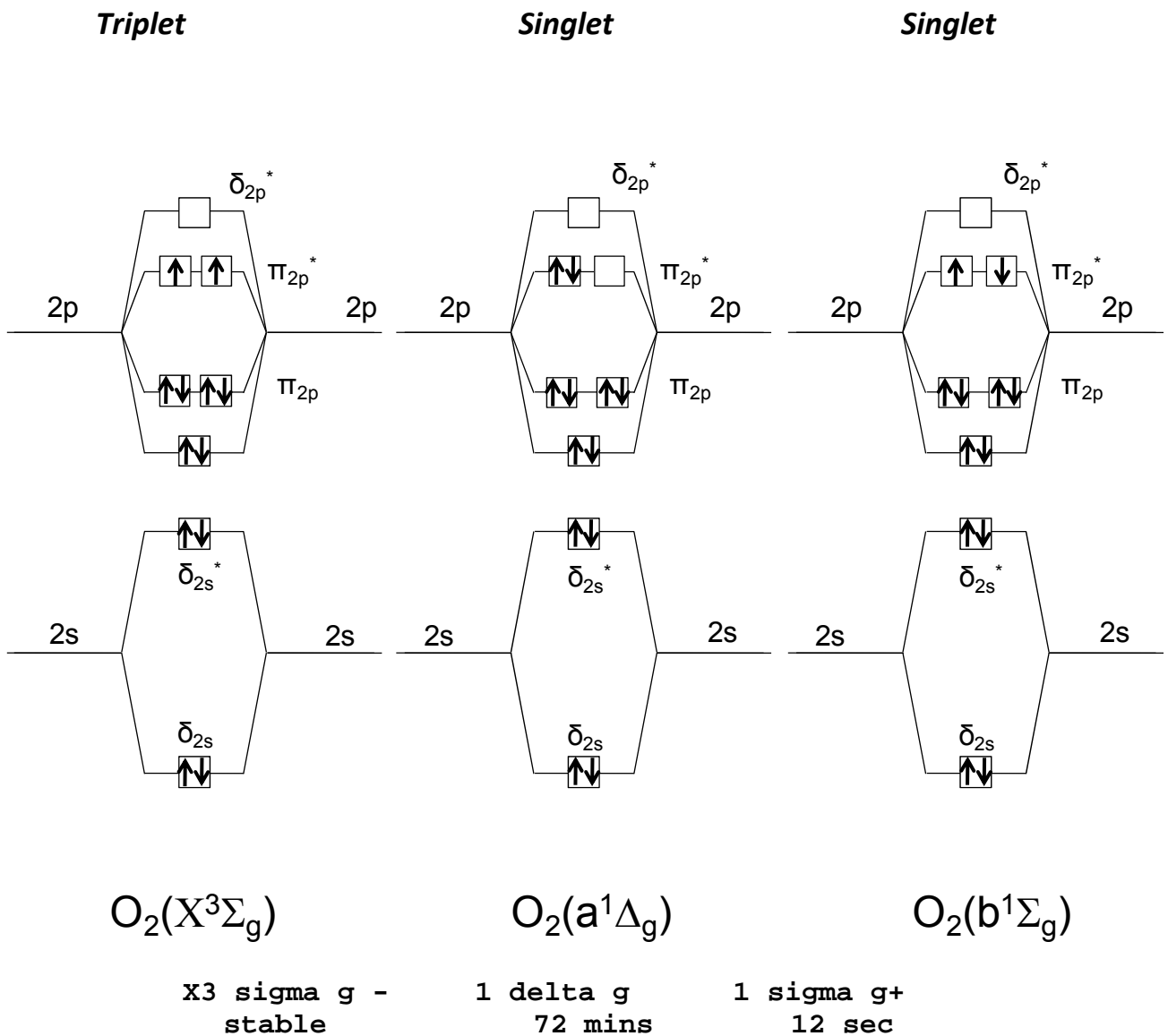
Clearly, O<sub>2</sub> does not fit that category and its absorption far in the near IR at around 760 nm requires some explanation. This rests in the electronic nature of triplet O<sub>2</sub> which is shown in Figure 6 which illustrates the parallel spin electrons in the outer anti bonding  $\pi^*$  y and z\* orbitals (Ref 8).



**FIGURE 6. TRIPLET OXYGEN**

Figure 7 shows the triplet and two possible singlet states of molecular oxygen.

The lower energy magnetic triplet state is preferred by quantum mechanics.



**FIGURE 7. TRIPLET AND SINGLET OXYGEN**

Molecular Orbital Theory (Ref 9) predicts two low-lying excited singlet states  $O_2(a^1\Delta_g)$  and  $O_2(b^1\Sigma_g^+)$ . These electronic states differ only in the spin and the occupancy of oxygen's two degenerate antibonding  $\pi_g$ -orbitals. The  $O_2(b^1\Sigma_g^+)$ -state is very short lived and relaxes quickly to the lowest lying excited state,  $O_2(a^1\Delta_g)$ . Thus, it is the latter state, which is normally referred to as singlet oxygen. The energy difference between the lowest energy of  $O_2$  in the singlet state and the lowest energy in the triplet state is about 11340 Kelvin ( $T_e(a^1\Delta_g \leftarrow X^3\Sigma_g^-) = 7882 \text{ cm}^{-1}$ ,

94.3 kJ/mol.) Molecular oxygen differs from most molecules in having an open-shell triplet ground state,  $O_2(X^3\Sigma_g^-)$ .

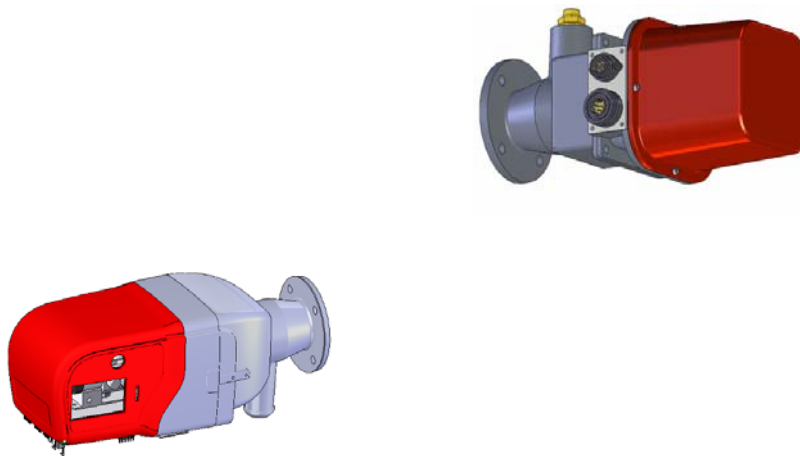
The electric dipole forbidden  $O_2$  A-band  $b^1\Sigma_g^+ \rightarrow X^3\Sigma_g^-$  transition (i.e. the electronic transition between the least stable singlet state and the triplet state) results in the measurable absorption of molecular oxygen at wavelengths around 760 nm (ref 10,11) The transition is often described as not just forbidden but highly forbidden.

Quantum mechanics deals in probabilities and uncertainties. The transition is highly improbable but not impossible. The common description does, however, indicate another surprising aspect of the properties of molecular oxygen.

### **X STACK /IN SITU TDL O<sub>2</sub>**

TDLs are available at the appropriate wavelengths for oxygen measurement and, indeed, oxygen has been frequently measured by TDLs since the mid 1990s, primarily replacing or complementing zirconia measurements for combustion control.

For this application, the arrangement is usually “X –stack “where the laser source is placed on one side of the flue stack and the receiver on the other (Figure 8). Sensitivity obtainable is directly proportional to path length ( in that sense wide stacks are good) but alignment is the other side of that coin. The wider the stack, the more difficult it is to align the laser source and receiver.



**FIGURE 8. X STACK TDL ANALYZER**

Purge gas is used on both units to isolate the optics from both the heat and particulate nature and corrosiveness of stack gas. The method is consequently a genuine “no contact” analytical method.

It differs fundamentally from zirconia analyzers also in the sense that it is a space rather than point measurement. There are advantages to either technology.

## **EXTRACTIVE TDL O<sub>2</sub>**

Absorption characteristics are, via collisional broadening, affected by pressure changes. The In situ approach tends to be limited to industrial combustion processes where pathlengths tend to be appreciable (and therefore sensitivity adequate), and the pressure is close to one bar absolute. The extractive approach, where pressure and pathlength are controllable, is increasingly being used to replace delicate paramagnetic devices for process O<sub>2</sub> measurement.



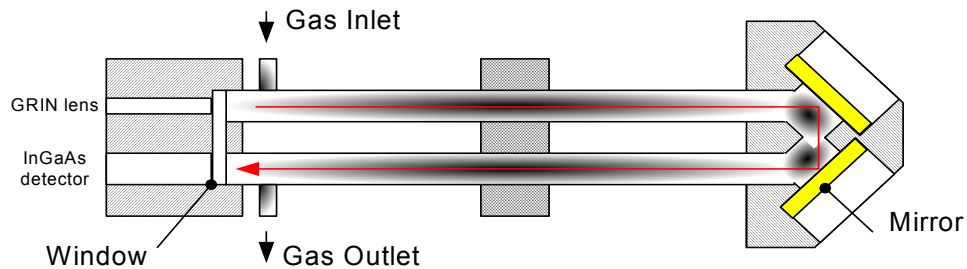
**FIGURE 9. EXTRACTIVE TDL ANALYZER**

Figure 9 illustrates a typical extractive TDL unit with the laser(s) and electronics to the left and the cell (multiple cells and lasers may be used) to the right, located in an enclosure that may be heated to minimize sample conditioning.

There are three fundamental benefits of TDL over paramagnetic techniques.

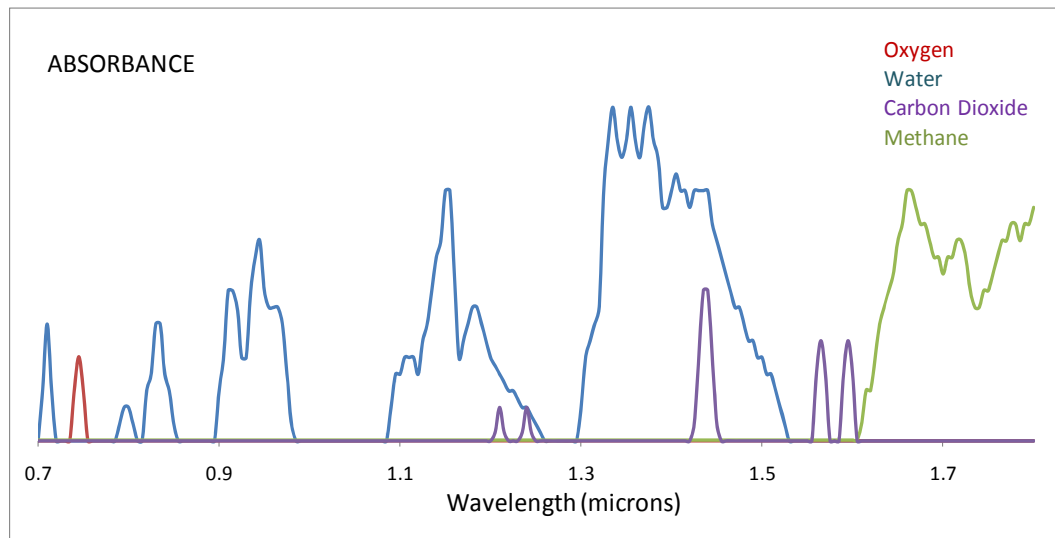
The gas sample does not make contact with fragile components (Figure 10). The laser beam occupies only a small part of the volume of the sample cuvette (typically 2 mm diameter) and the tuneable methodology does not require high percentage transmission of the signal. Sample conditioning is chosen to minimise condensation of liquids or particulates within the sample cell, but the set up is tolerant of contamination and the cell, in the event of major upset, is cleanable

without spare parts other than gasket material. The cuvette itself is not required to be reflective and may, in principle, be made of any appropriate material.



**FIGURE 10. TDL MEASURING CELL**

Cross interference is a minimal concern for TDL O<sub>2</sub> measurement as the EM spectrum in the 760 nm region is relatively clear (Figure 11)

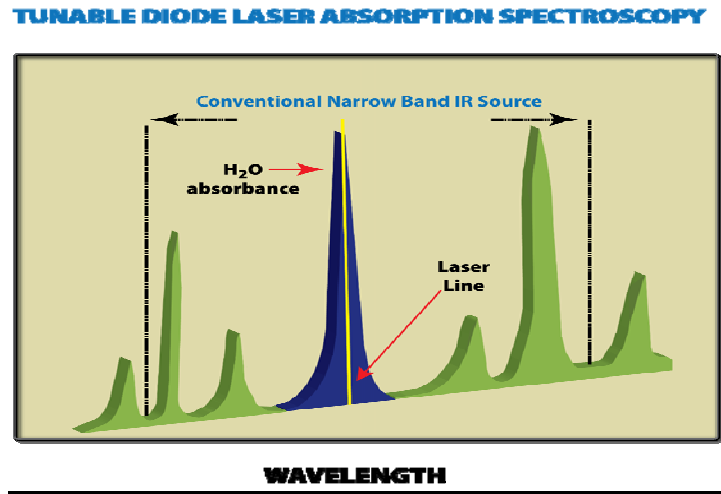


**FIGURE 11. NEAR INFRARED O<sub>2</sub> SPECTRUM AND ABSORPTION WAVELENGTHS OF SOME COMMON GASES.**

The detection mechanism for TDL technology is usually based on a form of Wavelength Modulation Spectroscopy (WMS). The first versions have been second harmonic (2f) analogue measurements through lock in amplifiers. The use of digital signal processing and increasingly sophisticated methodologies continue to improve sensitivity and discrimination.

A fundamental property of the methodology, which distinguishes it from conventional process photometry, is the ability of the laser to be scanned across a narrow absorption peak repeatedly and rapidly (a number of times per second) by changing the current through the laser. Thus the

baseline and peak are continuously measured which effectively allows ongoing recalculation of the background or zero. TDL analyzers have been shown to be capable of effective, accurate measurement even when 95% of the original signal has been lost.



**FIGURE 12. TYPICAL BANDWIDTHS IN CONVENTIONAL AND TDL ANALYSIS**

*Analyte, typical absorption line width 0.05 nm*  
*Laser scan range, typically 0.2 - 0.3 nm,*  
*Laser spectral line width is ca. 0.0001 nm*  
*Conventional optical filter bandwidth > 5 nm*

Ruggedness and lack of frequent zero requirement thereby improve this technique over paramagnetic sensor use.

A further recent development enhances both the accuracy of TDL and calibration stability.

TDLs could operate in terms of their wavelength tunability by changing their temperature. Current change allows less wavelength flexibility but is a more practically rapid approach for a process analyzer. The very narrow wavelength band of the laser and its narrow focus on a rotational peak characteristic (Figure 12) means that it is easy for the laser to “lose” the analyte peak, especially where absorption is weak and the analyte concentration is small.

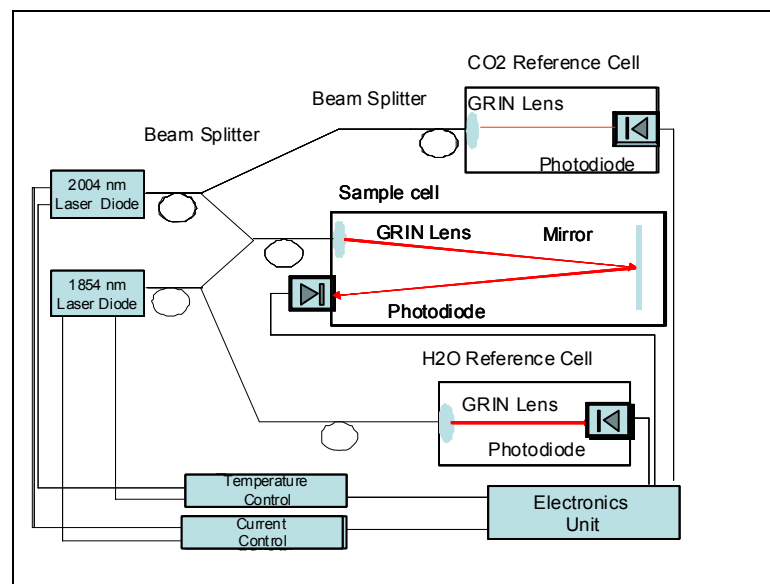
Inaccurate results due to this “peak locking” issue have been common (but not always recognised or admitted) in some TDL applications, particularly low level H<sub>2</sub>O, CO and H<sub>2</sub>S measurement.

A solution to this is to include in the analysis a reference cuvette of known concentration of analyte (Figure 13). (Ref 12, 13)

The illustration shows two reference cells for a dual measurement TDL. TDL measurement is limited to relatively light gases, which have some rotational fine structure. CO<sub>2</sub>, H<sub>2</sub>S, H<sub>2</sub>O, CH<sub>4</sub>, CO and NH<sub>3</sub> are increasingly common measurements in addition to O<sub>2</sub>.

The sample and reference cells each contain 0.5mm<sup>2</sup> InGaAs-photodiode detectors, which are connected to separate input channels of the electronics unit. With this configuration, it was possible to make simultaneous measurements of unknown samples and known references, which were used to lock the output wavelengths for both lasers.

Reference cells containing water vapor and carbon dioxide in a 10.0 cm path length were used to lock the output wavelength of the corresponding laser diodes. Each of the sealed reference cells contained a known concentration of the analyte in a host gas, which had no absorbance in the spectral range of interest. Two nested levels of temperature control were employed to maintain the operation of the lasers at the proper wavelength. The first level is a simple PID control loop, which maintained the laser at a target temperature. In the second level, the outer control loop, the spectra of the analyte samples in the reference cells were monitored. Minor shifts in the observed peak positions were used as a feedback signal for the temperature set point of the inner control loop. Thus, the outer-control loop provides a fine adjustment for the inner-control loop.



**FIGURE 13. TYPICAL DUAL REFERENCE CELL SYSTEM**

An additional, and significant, benefit of this method is that known “span” concentrations of analyte are now included in the system and these are used for validation of the reading. The potential to use air as a reference for % O<sub>2</sub> level measurement is, of course, particularly convenient.

The technology consequently approaches a position where calibration is very stable and the need for it minimized.

The increased precision of digital data processing, to which the reference cell data contributes, allows more precise spectral interpretation than conventional analogue 2f data manipulation,

which leads to an improved ability to measure additional components within the tuning scan of a single laser. The remote spectral location of the near IR O<sub>2</sub> absorption on the one hand makes measurement likely to be interference free, but on the other is very limiting in terms of single laser multi-component measurements. Typically, a multi measurement TDL analyser would need two TDL units, where the non-oxygen laser may, in the right circumstances, be able to measure additional components. A single dual laser analyzer can measure O<sub>2</sub> and CO on combustion processes

Oxygen is not a strong near IR absorber and the sensitivity for standard units enables measurement in the percentage range. Cell path lengths of order 0.5 to 1m metre will, for process O<sub>2</sub> measurements, allow sensitivities, which are very comparable to those of paramagnetic sensors, with lower detection limits (LDLs) down to 100 ppm O<sub>2</sub>. It is possible to consider greater sensitivity by increasing the path length, which in practice is achieved by using multi pass Herriot cells.

## SUMMARY AND CONCLUSIONS

Paramagnetic Oxygen analyzers (POAs) continue to be widely used for Process Oxygen gas analysis. The sensors, though, are relatively expensive devices to replace and the nature of their use, particularly on dirty or potentially condensing samples, may make the frequency of replacement unacceptable (See figure 3). For this reason, POAs were largely replaced (very rapidly) for combustion waste gas analysis when zirconia O<sub>2</sub> analyzers appeared in the late 1960's.. The TDL for O<sub>2</sub> measurement has now replaced many zirconia analyzers. This TDL "space" measurement is likely to co-exist with the zirconia "point" measurement as a matter of application and cost preference. TDL for process O<sub>2</sub> applications will become increasingly applied as a method of equivalent accuracy and similar cost to paramagnetic, but with reduced maintenance and spares cost. Improved data processing methods will increasingly enable single analyzers to measure O<sub>2</sub> and one or more IR absorbing gases on a single analyzer.

## REFERENCES

1. Lavoisier, A. Elements of Chemistry. Dover Publications. New York. 1965. First Published, Paris 1789.
2. Brown G, The Energy Of Life Harper Collins. London 1999.
3. Oxygen, The Molecule that made the World, Nick Lane. Oxford University Press 2002.
4. IUPAC Compendium of Chemical Technology. Internet Edition, "Configuration Electronic " and "Aufbau Principle ".
5. Curl, Robert and Tittel, Frank, "Tunable Infrared Laser Spectroscopy", Annual Report on the Progress of Chemistry, Section C Physical Chemistry, Royal Society of Chemistry, Vol. 98, 2002, pp. 219–272.

6. Linnerud, I., Kaspersen P and Jaeger, T., “Gas Monitoring in the Process Industry Using Diode Laser Spectroscopy”, Applied Physics B, Vol. 67, 1998, pp. 297-305.
7. Webster, Christopher, Menzies, Robert, and Hinkley, David, “Infrared Laser Absorption: Theory and Applications”, Laser Remote Chemical Analysis, Vol. 94, John Wiley & Sons, New York, New York, 1988, pp. 163–273.
8. O<sub>2</sub> Triplet Diradical .The Chemogenesis Web Book Internet Edition.
9. MO Theory Spectroscopy.Molecular Orbitals and Chemical Bonding. Robert Mulliken. 1966 Nobel Lecture
10. Wilkinson F Helman W and Ross A, (1995). Rate Constants for the Decay and Reactions of the Lower Electronically Excited Singlet State of Molecular Oxygen in Solution. .Journal of Physical and Chemical Reference Data 24 (2) : 622 -677
11. IUPAC Compendium of Chemical Terminology.The Gold Book. McNaught and Wilkinson. Blackwell Scientific Publications, Oxford.1997
12. Amerov , Fiore and Maskas, Meyer, New Gas analyzer for the Measurement of Water Vapor Concentrations.. ISA Analysis Division 52<sup>nd</sup> Symposium Proceedings. Instrumentation Systems and Auto Soc. Houston ,Texas 2007/8.
13. Amerov, Fiore and Langridge. Process Gas Analyzer for the Measurement of Water and Carbon Dioxide Concentrations.ISA Analysis Division 53<sup>rd</sup> Symposium Proceedings 2009